PATENT ABSTRACTS OF JAPAN

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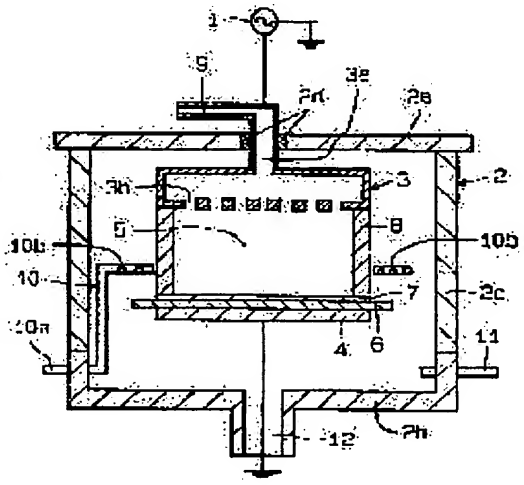
(54) SURFACE TREATMENT OF SUBSTRATE

(57)Abstract:
PURPOSE: To provide the method for surface treatment of a substrate by a glow discharge plasma method under an atm. pressure by which gases for reaction are uniformly diffused and supplied to a plasma region and with which the use efficiency thereof is good.
CONSTITUTION: The substrate 7 is installed into the space of a plasma generator which is constituted by providing one surface of a metallic electrode 4 with a first solid dielectric substance 6, disposing a porous metallic electrode 3 opposite to this first solid dielectric substance 6, forming the porous metallic electrode 3 so as to permit the supply of the gases for reaction thereto and forming a space covered with a second solid dielectric substance 8 at its flanks between the first solid dielectric substance 6 and the porous metallic electrode 3. The gases for reaction and an inert gas are supplied to the substrate 7 and the glow discharge plasma is generated under the pressure approximate to the atm. pressure. The excited active species are brought into contact with the substrate surface.



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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The 1st solid dielectric is prepared in the whole surface of a metal electrode, and counter with the 1st solid dielectric and a porous metal electrode is prepared. It is supposed that supply of the gas for a reaction is possible for a porous metal electrode, and a substrate is installed between the 1st solid dielectric and a porous metal electrode in the space covered with the 2nd solid dielectric of the plasma generator made into the space where the side face was covered with the 2nd solid dielectric. While supplying inert gas to a substrate, the gas for a reaction is supplied to a substrate through a porous metal electrode. Under the pressure near the atmospheric pressure The surface treatment approach of the substrate characterized by contacting the active species which gave the electrical potential difference to the electrode, was made to generate the glow discharge plasma, and was excited by the plasma on a substrate front face.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the surface treatment approach of the substrate by the plasma near the atmospheric pressure in more detail about the surface treatment approach of substrates, such as plastics, paper, a metal, glass, and ceramics.
[0002]
[Description of the Prior Art] Before, the surface treatment approach by the low-pressure glow discharge plasma of 0.1 - 10Torr extent is widely learned as the approach of wettability control of the front face of substrates, such as plastics, paper, a metal, glass, and ceramics, or surface qualification, and, also industrially, it is applied. In this surface treatment approach, if it becomes a high pressure from the above-mentioned pressure, since discharge becomes local, it will shift to arc discharge and utilization to heat-resistant scarce plastics or a substrate like paper will become difficult, the above-mentioned pressure range is usually chosen so that it can apply to all substrates. For this reason, on the need of making it a vacuum (or low voltage), the container for processing needs an expensive vacuum chamber, and evacuation equipment is needed. Furthermore, if it is going to process to the substrate of a large area in order to process in a vacuum, a mass vacuum housing is needed and a large-sized thing is required also for evacuation equipment. Therefore, there was a trouble that facility costs became high. Moreover, when surface treatment of a substrate with high water absorption was performed, long duration was taken to make it a vacuum and there was also a trouble that a processing article became cost high.
[0003] Then, in order to conquer the above-mentioned various troubles, the glow discharge plasma under the atmospheric pressure in which the processing to a large area substrate is possible has been proposed as low cost-ization of equipment and a facility. For example, the surface treatment approach of performing the glow discharge plasma to JP,2-15171,A under atmospheric pressure by the approach of using a thin line mold electrode for JP,2-48626,B by the approach of arranging a solid dielectric in an electrode surface is proposed. Although the approach of supplying two or more puncturing to the plasma region near [a perforated pipe to] the substrate which it has was used by these proposals in the mixed gas of the inert gas and the gas for a reaction which are mainly concerned with helium, when it became the substrate of a large area in this case, there was a trouble that it was difficult for homogeneity to carry out diffusion supply of the gas.
[0004] Moreover, it considers as the metal electrode which can supply the reactant gas for surface treatment which arranged the perforated plate-like solid dielectric in the opposed face for one side to JP,2-73979,A. A substrate is installed between two electrodes which used another side as the metal electrode and which counter, and inert gas and the gas for a reaction are supplied to inter-electrode space. Under the pressure near the atmospheric pressure Give an electrical potential difference to an electrode, the glow discharge plasma is made to cause, and the thin film forming method by contacting the active species excited by the plasma on a substrate front face is proposed. However, by this approach, there were few rates of the gas actually used for surface treatment among the gas for a reaction, intact gas occurred so much, and there was a trouble that the utilization ratio (yield) of the gas for a reaction was bad.
[0005]
[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned trouble, and the object has gas for a reaction in homogeneity in a plasma region that diffusion supply is carried out and the utilization ratio offers the surface treatment approach of the substrate by the good glow discharge plasma

method under atmospheric pressure.
[0006]
[Means for Solving the Problem] As for the surface treatment approach of the substrate of this invention, the 1st solid dielectric is prepared in the whole surface of a metal electrode. Counter with the 1st solid dielectric, a porous metal electrode is prepared, and supply of the gas for a reaction of a porous metal electrode is enabled. Between the 1st solid dielectric and a porous metal electrode, while a side face installs a substrate in the space covered with the 2nd solid dielectric of the plasma generator made into the space covered with the 2nd solid dielectric and supplies inert gas to a substrate The gas for a reaction is supplied to a substrate through a porous metal electrode, an electrical potential difference is given to an electrode under the pressure near the atmospheric pressure, the glow discharge plasma is generated, and it is characterized by contacting the active species excited by the plasma on a substrate front face.
[0007] In this invention, mainly by forming formation of a surface functional group layer, formation of a free radical layer, a hydrophilic property, and a water-repellent thin film etc., the surface preparation of a substrate controls the surface energy of a substrate, makes the thin film of minerals or the quality of organic form in reforming the wettability and the adhesive property of a substrate, and a substrate front face, and points out chemical, mechanical, optical, and giving electrical characteristics etc. to a substrate.
[0008] In this invention, the gas for a reaction chosen according to the object of surface treatment is supplied to a plasma region from a porous metal electrode, and surface treatment is performed. In making a substrate front face carry out the chemical bond of the fluorine, making surface energy low as gas for a reaction, for example and giving water repellence, it uses the gas of fluorine content. As fluorine content gas, sulfur fluoride gas, such as saturation fluoride [carbon] gas, such as 6 4 fluoride [carbon] (CF4), carbon, etc. fluoride (C two F6), and 6 sulfur fluorides (SF6), is mentioned.
[0009] Moreover, when making surface energy high and giving a hydrophilic property to reverse, in order to make the layer which has functional groups, such as a carbonyl group, hydroxyl, and an amino group, form in a front face, the gas of a hydrocarbon compound is used. As the above-mentioned hydrocarbon compound, for example Methane, ethane, a propane, Alkanes, such as butane, a pentane, and a hexane; Ethylene, a propylene, Alkadiene, such as alkenes; pentadienes, such as a butene and a pentene, and a butadiene; Acetylene, Alkynes, such as methylacetylene; Benzene, toluene, a xylene, Aromatic hydrocarbon, such as an indene, naphthalene, and a phenanthrene; A cyclopropane, Cycloalkanes, such as a cyclohexane; Cycloalkene; methanols, such as cyclopentene and a cyclohexene, Alcohols, such as ethanol; aldehydes, such as ketones; methanals, such as an acetone and a methyl ethyl ketone, and ethanal, are mentioned, and these may be used independently and may be used together two or more sorts. Moreover, it is also possible to use oxygen gas, the mixed gas of oxygen and hydrogen, a steam, ammonia gas, etc. in this case.
[0010] in order [moreover, / chemical to a substrate mechanical, optical, and in order to give electrical characteristics etc.] -- SiO2, TiO2, and SnO2 etc. -- when forming a metallic-oxide thin film, the gas or the steams of an organic metal compound, such as hydrogenation metal gas, halogenation metal gas, or a metal alcoholate, are used.
[0011] Construction material, especially a configuration, etc. are not limited, but even when plastics, a metal, glass, a ceramic, paper, fiber, etc. are mentioned and the substrate used for this invention has them, porosity is also available for it. [precise] As plastics, a film or sheets, such as polyethylene terephthalate and polyethylenenaphthalate, can be used, for example. [, such as polyester; polyethylene or polypropylene,] [, such as a polyolefine; polystyrene; polyamide; polyvinyl chloride; polycarbonate; polyacrylonitrile,] In the case of a film, what was extended may also be a non-extended thing. Moreover, what performed well-known processing of surface washing or surface-activity-izing may be used.
[0012] Based on drawing, this invention is explained to an example for the case where water repellence is given to below on the surface of plastics at a detail. In addition, in drawing 1 -3, the same sign is given to what corresponds mutually. Drawing 1 is type section drawing showing an example of the plasma generator used for this invention. This equipment consists of a power supply section 1, a processing container 2, the porous metal electrode 3 which counters and a metal electrode 4, and the two inter-electrode plasma treatment sections 5 that counter. For it being supposed that impression of the electrical potential difference of the frequency of kHz order is possible for a power supply section 1, and giving water repellence, the frequency of 10-30kHz is desirable. Since the behavior which shifts to arc discharge is shown when it takes [processing] time amount

and is inefficient and too hig[redacted]nce a plasma consistency and self-bias [redacted]become small if applied voltage is too low although impression of high tension performs plasma formation, it is desirable to impress an electrical potential difference so that it may become field strength 5 - 40 kV/cm extent.
[0013] Top-face 2a and base 2b is [product made from stainless steel and side-face 2c] the products made from Pyrex glass, and, as for the processing container 2, 2d of insulators is arranged between top-face 2a and the porous metal electrode 3. Glass and the product made from plastics are sufficient not only as this but all, and if the construction material of the processing container 2 has taken the electrode and the insulation, metal, such as stainless steel and aluminum, is sufficient as it.
[0014] In this invention, the plasma treatment section 5 by the glow discharge plasma is the space between the 1st solid dielectric and a porous metal electrode. The electrode which counters uses at least one side as the metal electrode which arranged the 1st solid dielectric in the opposed face, and uses at least one side as the porous metal electrode which can supply the gas for a reaction. That is, there are the following five cases as a configuration of two electrodes which counter.
** The porous metal electrode of porous metal-electrode-solid dielectric arrangement of porous metal-electrode-porosity metal-electrode ** solid dielectric arrangement of porous metal-electrode ** solid dielectric arrangement of porous metal-electrode ** metal-electrode-solid dielectric arrangement of metal-electrode-solid dielectric arrangement of metal-electrode-porosity metal-electrode ** solid dielectric arrangement of solid dielectric arrangement [0015] At drawing 1 , the configuration of the above-mentioned ** is shown and two electrodes which counter consist of a porous metal electrode 3 and a metal electrode 4 which arranged the 1st solid dielectric 6. As the porous metal electrode itself serves as the supply pipe of gas and the porous metal electrode which can supply the gas for a reaction shows it to the porous metal electrode 3 of drawing 1 , path 3a of gas is prepared in the interior of an electrode, and the opposed face to the electrode of another side which counters is made into the porous field which has puncturing 3b of a large number used as the outlet section of gas. In addition, the porous metal electrode 3 and a metal electrode 4 are connected so that either may be an anode plate side and another side may be on a cathode side. Moreover, as for two electrodes with which the configuration of the above-mentioned ** - ** counters, whichever may become the upper part or the lower part.

[0016] A plastic plate 7 is placed on the 1st solid dielectric 6. In addition, if the surface treatment of only one side of a substrate is required, ** - ** will be chosen among the configurations of the aforementioned electrode, and if double-sided simultaneous processing is required, the configuration of ** or ** will be chosen.
[0017] As construction material of the 1st solid dielectric 6, plastics, such as ceramic; glass; polytetrafluoroethylene and polyethylene terephthalate, is used, and it is suitably chosen by reactivity with the gas for a reaction. For example, since glass melts easily by 4 fluoride [carbon] plasma, in water-repellent grant, it is hard to use. Since it will be hard coming to discharge as a configuration if too thick [if too thin, dielectric breakdown will happen at the time of high-tension impression, and arc discharge will arise, and] although the shape of the shape of a sheet and a film is also available, the thickness of 0.04-4mm is desirable. Since arc discharge will arise into the part if there is a part which is not arranged in a part of opposed face, arrangement of a solid dielectric needs to be arranged all over an opposed face.
[0018] The homogeneity of diffusion of the gas of the space between the 1st solid dielectric which will counter if too long although suitably determined by the quantity of gas flow of the gas for a reaction, the magnitude of applied voltage, the thickness of a processing substrate, etc., and a porous metal electrode is spoiled, and its intact gas for a reaction increases, and since the distance between the 1st solid dielectric which counters, and a porous metal electrode is inefficient-like, it is desirable. [of 1-20mm]
[0019] as [show / in drawing 1 / as arrangement structure of the 1st solid dielectric which counters, and a porous metal electrode] -- coaxial-circles telescopic, a cylinder pair plate mold, a hyperboloid pair plate mold, etc. may be mutually used besides a parallel plate mold -- as it carries out, you may have the shape of two or more pipe as the point of one electrode shows drawing 2 , and shown in drawing 3 , you may have the shape of two or more thin line.
[0020] Pure metals, such as a metal of multicomponent systems, such as stainless steel and brass, or copper, and aluminum, are also available for the construction material of a metal electrode.
[0021] In this invention, the side face between the 1st solid dielectric which counters, and a porous metal electrode is covered with the 2nd solid dielectric 8. although the thing same as construction material of the 2nd

solid dielectric as the constru[redacted] material used for said 1st solid dielec[redacted] carried out is mentioned -- the 1st solid dielectric -- being the sa[redacted] -- you may differ by carrying out. As an approach of covering the side face between the 1st solid dielectric which counters, and a porous metal electrode As shown in drawing 1 , when the 2nd solid dielectric has remarkable thickness like a sheet It is in the condition which enabled it to go into ******. the processing schedule field of the substrate processed since processing of the substrate front face in contact with the 2nd solid dielectric becomes impossible -- large -- a sheet -- **** omission and the processing schedule field of a substrate -- ****** -- him -- As this sheet is shown in the approach, drawing 2 , or drawing 3 put between the 1st solid dielectric which counters, and a porous metal electrode, when the 2nd solid dielectric is a film, the approach of twisting around the peripheral face of an electrode in the shape of a skirt board is mentioned.

[0022] The gas for a reaction is efficiently used so that it will be carried out with the 2nd solid dielectric, if the side face between the 1st solid dielectric and a porous metal electrode is sealed, but to supply inert gas and the gas for a reaction to the processing container 2 from a different entry, in order to make the plasma treatment section 5 diffuse inert gas, it is necessary to open sufficient clearance. Case [whose approach and 2nd solid dielectric 8 which open a small hole in the side face of the 2nd solid dielectric 8, for example are / like the above-mentioned sheet as an approach of making a clearance forming], the method of preparing irregularity in a sheet top face or an underside etc. is mentioned.

[0023] In this invention, as mentioned above, a substrate 7 is installed between said 1st solid dielectric and porous metal electrodes, inert gas and the gas for a reaction are supplied to said space, give an electrical potential difference to an electrode, the glow discharge plasma is made to cause under the pressure near the atmospheric pressure, and the active species excited by the plasma is contacted on a substrate front face.

[0024] Atmospheric pressure is desirable, when the pressure the above and near the atmospheric pressure points out the thing of 100 - 770Torr and low cost-ization of equipment and a facility is taken into consideration.

[0025] As inert gas, although the simple substance or mixed gas of rare gas, such as helium, Ne, Ar, and Xe, or nitrogen gas is used, it is desirable to use helium advantageous to the life of a metastable state understanding the gas for a reaction an excited part for a long time. To use inert gas other than helium, it is necessary to mix hydrocarbon gas, such as organic substance steams, such as an acetone within 2 volume %, and a methanol, and methane, ethane.

[0026] When giving water repellence, the gas of fluorine content is used as gas for a reaction. Since it is hard to generate the glow discharge plasma even if fluorine content gas concentration impresses high tension above about 10 volume %, below about 10 volume % is desirable, the mixing ratio of inert gas and fluorine content gas has little amount of the reactant gas used, and between 0.3 which can end and can give water repellence - 5.0 volume %s is more desirable.

[0027] Control of flow of the gas for a reaction is carried out with a massflow controller, and it is introduced into the plasma treatment section 5 from the gas inlet 9 of the porous metal electrode 3. From gas inlet 10a of the gas installation tubing 10, by the massflow controller, control of flow of the inert gas is carried out, and it is introduced into the processing container 2. Although it is made for the part in the processing container 2 to have the perimeter of the plasma treatment section 5 surrounded as shown in drawing 1 and many holes may be set to gas outlet 10b in an open eclipse and its hole at the inner skin of the surrounded part, especially, the gas installation tubing 10 is not constituted in this way, but ** also diffuses inert gas for it in homogeneity mostly at the plasma treatment section 5. Moreover, although inert gas and the gas for a reaction may be mixed and you may introduce from a gas inlet 9, in order to give water repellence to homogeneity, it is desirable to introduce only the gas for a reaction from a gas inlet 9. In addition, the intact gas for a reaction and inert gas are discharged from the gas exhaust port 11 of a processing container.

[0028] To the atmospheric pressure plasma treatment of water-repellent grant, it is unnecessary and especially heating and cooling of a substrate are possible enough under a room temperature.

[0029] Moreover, even if the processing time is determined in the magnitude of applied voltage, it ****** in about 5 seconds in the range of said applied voltage and it processes over the time amount beyond it, water-repellent ****** does not improve but short-time processing is enough as it.

[0030]

[Example] Hereafter, the example of this invention is explained.

The plasma generator shown in example 1 drawing 1 (a metal electrode 4 is used as a disk mold with a diameter

of 80mm, and arranges polyt[redacted]luoroethylene with a diameter [of 90m[redacted], and a thickness of 1mm as the 1st solid dielectric 6 on it.) the porous metal electrode 3 -- a disk mold with a diameter [of an opposed face] of 80mm -- setting -- as a substrate 7 -- polyester film (the Toray Industries, Inc. make --) with a 80mmx80mmx thickness of 100 micrometers A trade name "lumiler S10" is placed on the 1st solid dielectric 6. On the substrate 7 The polytetrafluoroethylene sheet of the shape of a corrugated plate with the outer diameter of 80mm, a bore [of 70mm], and a thickness of 5mm is placed for the side face between the 1st solid dielectric which counters, and a porous metal electrode as the 2nd solid dielectric 8 of a wrap (since a sheet is a corrugated plate-like). It is an oil sealed rotary pump (not shown) to 1Torr after setting the distance of the substrate 7 and the porous metal electrode 3 with which few clearances are formed between a substrate 7 and the 2nd solid dielectric 8 and between the porous metal electrode 3 and the 2nd solid dielectric 8 as about 5mm. the following -- being the same -- it exhausted from the exhaust port 12.

[0031] Subsequently, after introducing 4 fluoride [carbon] gas of quantity-of-gas-flow 2sccm in the processing container 2 from gas inlet 10a and making helium gas of 198sccm into the atmospheric pressure of 760Torr for it more nearly again than a gas inlet 9, the square wave with a frequency of 15kHz was impressed with power (6.2kV and 28mA), was left for 10 seconds, and surface treatment of a substrate was carried out. As a result of observing plasma luminescence and observing the voltage-current property at that time with an oscilloscope with high-tension impression, the pulse characteristics shown in drawing 4 were shown, and it turned out that it is the typical pulse discharge of the current characteristic of a single pulse at the half cycle.

[0032] Next, contact angle measurement to the pure water of the processing side of the substrate after processing was performed. Consequently, it was clear for 100 - 108 degrees to be shown and to ****** by the circular region with a diameter of 60mm. In addition, the contact angle of the used substrate was 65 degrees. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, it turned out that 67% of fluorine is carrying out the chemical bond to the front face by the atomic ratio.

The polytetrafluoroethylene sheet of the shape of a corrugated plate with a thickness of 5mm was used as the 2nd solid dielectric 8 in example 2 example 1, And the thing for which the polytetrafluoroethylene sheet of the shape of a corrugated plate with a thickness of 10mm was used instead of having set the distance of a substrate 7 and the porous metal electrode 3 as about 5mm, respectively, And everything but having changed the quantity of gas flow in an example 1, power, and the processing time as follows carried out surface treatment of a substrate to having set the distance of a substrate 7 and the porous metal electrode 3 as about 10mm, and a list like the example 1. After introducing 4 fluoride [carbon] gas of quantity-of-gas-flow 6sccm in the processing container 2 from gas inlet 10a and making helium gas of 194sccm into the atmospheric pressure of 760Torr for it more nearly again than a gas inlet 9, the square wave with a frequency of 15kHz was impressed with power (10.0kV and 35mA), was left for 10 minutes, and surface treatment of a substrate was carried out.

[0033] Consequently, plasma luminescence was observed with high-tension impression, and it was clear the contact angle's over the pure water of the processing side of the substrate after processing for 100 - 108 degrees to be shown and to ****** by the circular region with a diameter of 60mm. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, it turned out that 65% of fluorine is carrying out the chemical bond to the front face by the atomic ratio.

[0034] The electrode of the structure shown in drawing 2 R> 2 to which the point of the example 3 porosity metal electrode 3 is carrying out the shape of two or more pipe (the opposed face of a porous metal electrode) Are a round shape with a diameter of 80mm and it is supposed that 80 with die-length [of 10mm], outer-diameter [of 2mm], and a bore of 1mm pipe 3c protrudes. A metal electrode 4 is used as a disk mold with a diameter of 85mm. As the 1st solid dielectric 6 on it The diameter of 90mm, The equipment which arranged polytetrafluoroethylene with a thickness of 1mm is used. as a substrate 7 -- a polyamide film (the Toray Industries, Inc. make --) with a 85mmx85mmx thickness of 12 micrometers A trade name "Kapton" is placed on the 1st solid dielectric 6. Subsequently, after covering the peripheral face of the porous metal electrode 3 in the shape of a skirt board with a polytetrafluoroethylene film with a thickness of 100 micrometers which is the 2nd solid dielectric 8 (die length from the opposed face of the porous metal electrode 3 to the head of a skirt board was set to 20mm), The distance to the head of pipe 3c of a substrate 7 and the porous metal electrode 3 was exhausted with the oil sealed rotary pump to 1Torr after setting it as about 5mm. Subsequently, after introducing 4 fluoride [carbon] gas of quantity-of-gas-flow 4sccm in the processing container 2 from gas inlet 10a and making the mixed gas of Ar gas of 194sccm, and the acetone steam of 2sccm(s) into the atmospheric

pressure of 760Torr for it mo[redacted]early again than a gas inlet 9, the squar[redacted]ve with a frequency of 15kHz was impressed with power (12.5k[redacted]and 38mA), was left for 10 seconds, and surface treatment of a substrate was carried out. Plasma luminescence was observed with high-tension impression.

[0035] It was clear the contact angle's over the pure water of the processing side of the substrate after processing for 100 - 108 degrees to be shown and to ****** by the circular region with a diameter of 85mm. In addition, the contact angle of the used substrate was 63 degrees. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, it turned out that 55% of fluorine is carrying out the chemical bond to the front face by the atomic ratio.

[0036] Having not placed the polytetrafluoroethylene sheet as the 2nd solid dielectric 8 of a wrap for the space between the 1st solid dielectric and a porous metal electrode on the substrate 7 in example of comparison 1 example 1, and 4 fluoride [carbon] gas from a gas inlet 9 Moreover, everything but having mixed 4 fluoride [carbon] gas and helium gas, and having introduced in the processing container 2 instead of [gas inlet 10a] having introduced helium gas in the processing container 2 from gas inlet 10a, carried out surface treatment of a substrate like the example 1.

[0037] Consequently, plasma luminescence was observed with high-tension impression, and, as for the contact angle over the pure water of the processing side of the substrate after processing, the contact angle of 30 or less degrees was found by not showing and ******(ing) in respect of all processings. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, it turned out that only about 5% of fluorine has carried out the chemical bond to the front face by the atomic ratio.

[0038] Instead of having mixed 4 fluoride [carbon] gas and helium gas in the example 1 of example of comparison 2 comparison, and having introduced in the processing container 2 from gas inlet 10a, everything but having introduced the mixed gas of 4 fluoride [carbon] gas and helium gas in the processing container 2 from the gas inlet 9 carried out surface treatment of a substrate like the example 1 of a comparison. Consequently, plasma luminescence was observed with high-tension impression, and, as for the contact angle over the pure water of the processing side of the substrate after processing, the contact angle of 35 - 45 degrees was found by not showing and ******(ing) in respect of all processings. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, it turned out that only about 20% of fluorine has carried out the chemical bond to the front face by the atomic ratio.

[0039] In the example 4 example 1, instead of having introduced helium gas for 4 fluoride [carbon] gas in the processing container 2 from gas inlet 10a more nearly again than a gas inlet 9, 4 fluoride [carbon] gas and helium gas were mixed, and everything but having introduced in the container carried out surface treatment of a substrate like [gas inlet / 9] the example 1. Consequently, the contact angle over the pure water of the processing side of the substrate after processing varied among 45 - 108 degrees. Moreover, as a result of analyzing a processing side by X-ray photoelectron spectroscopy, 20 - 60% of fluorine which carried out the chemical bond was checked by the atomic ratio.

[0040] In the example 5 example 1, everything but having used the filter paper performed surface treatment like the example 1 instead of having used polyester film as a substrate. Consequently, it was clear the contact angle's over the pure water of the processing side of the substrate after processing for 100 - 108 degrees to be shown and to ****** by the circular region with a diameter of 60mm.

[0041] The electrode of the structure shown in drawing 3 to which the point of the example 6 porosity metal electrode 3 is carrying out the shape of two or more thin line (the opposed face of a porous metal electrode) the diameter of 80mm -- circular -- 3d of thin lines with a die length of 10mm -- 10/cm2 It is supposed that it protrudes by the consistency. A metal electrode 4 is used as a disk mold with a diameter of 85mm. As the 1st solid dielectric 6 on it The diameter of 90mm, The equipment which arranged polytetrafluoroethylene with a thickness of 1mm is used. as a substrate 7 -- polyester film (the Toray Industries, Inc. make --) with a 85mmx85mmx thickness of 100 micrometers A trade name "lumiler S10" is placed on the 1st solid dielectric 6. Subsequently, after covering the peripheral face of a porous metal electrode in the shape of a skirt board with a polytetrafluoroethylene film with a thickness of 100 micrometers which is the 2nd solid dielectric 8 (die length from the opposed face of the porous metal electrode 3 to the head of a skirt board was set to 20mm), The distance to the head of 3d of thin lines of a substrate 7 and the porous metal electrode 3 was exhausted with the oil sealed rotary pump to 1Torr after setting it as about 5mm.

[0042] Subsequently, after introducing the mixed gas of 4 fluoride [carbon] gas of quantity-of-gas-flow 1sccm,

and the oxygen of 2sccm(s) [redacted] processing container 2 from gas inlet [redacted] and making helium gas of 197sccm into the atmospheric pressure of 760Torr for it more nearly again than a gas inlet 9, the square wave with a frequency of 15kHz was impressed with power (6.2kV and 28mA), was left for 30 seconds, and surface treatment of a substrate was carried out. Plasma luminescence was observed with high-tension impression. It was clear that the contact angle's over the pure water of the processing side of the substrate after processing 15 degrees is shown and hydrophilization is carried out by the circular region with a diameter of 85mm.
[0043]
[Effect of the Invention] Compared with the surface treatment approaches, such as plastics by the conventional low voltage glow discharge plasma, it does not need equipment and to be furnished for special vacuum formation, but the configuration of this invention is as above-mentioned, and handling is [moreover, the special actuation for it is also unnecessary, and it excels in the cost lowering effectiveness, and] easy. Moreover, since diffusion supply of the gas for a reaction is carried out in a plasma region at homogeneity, large-area-izing of the processing field which was the technical problem of the atmospheric pressure plasma is possible, and efficient utilization of the gas for a reaction is possible. Furthermore, moreover surface treatment is simultaneously possible in both sides of a substrate, the block definition of a processing side is also possible and the repercussion effect on industry will be large from now on. Furthermore, it can develop easily also to thin film formation.

[Translation done.]

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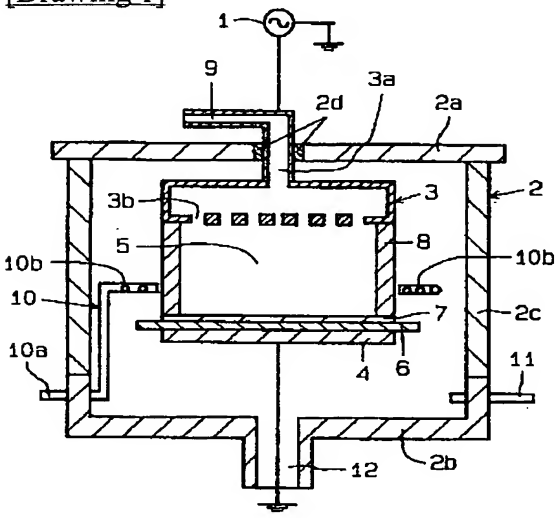
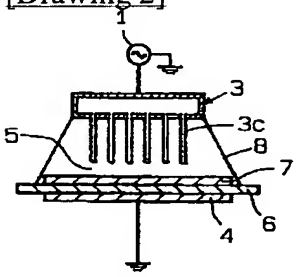
DRAWINGS

[Drawing 1]



[Drawing 2]



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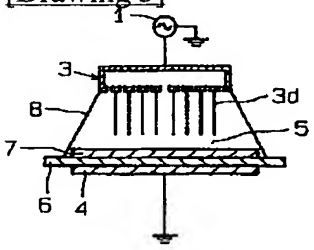

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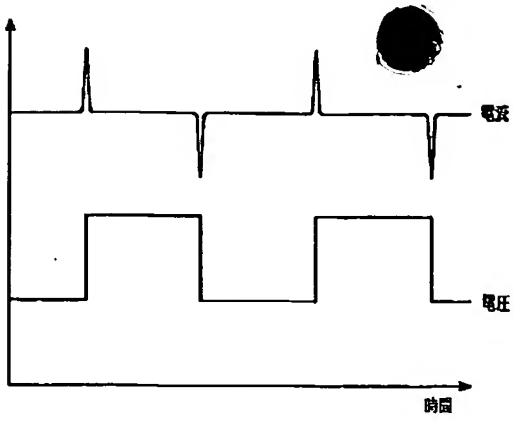

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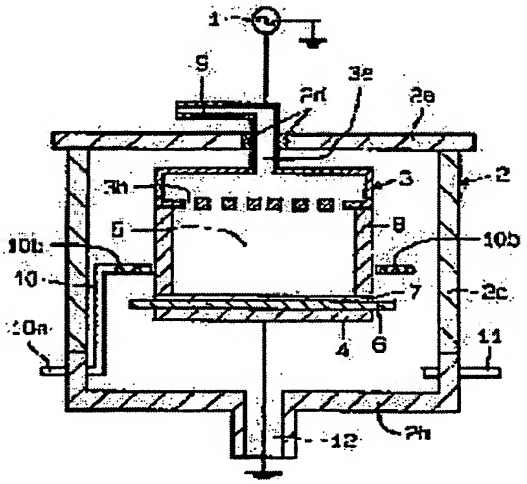
(72)Inventor : YUASA MOTOKAZU
KAWAI SHIGEMASA

(54) SURFACE TREATMENT OF SUBSTRATE

(57)Abstract:
PURPOSE: To provide the method for surface treatment of a substrate by a glow discharge plasma method under an atm. pressure by which gases for reaction are uniformly diffused and supplied to a plasma region and with which the use efficiency thereof is good.
CONSTITUTION: The substrate 7 is installed into the space of a plasma generator which is constituted by providing one surface of a metallic electrode 4 with a first solid dielectric substance 6, disposing a porous metallic electrode 3 opposite to this first solid dielectric substance 6, forming the porous metallic electrode 3 so as to permit the supply of the gases for reaction thereto and forming a space covered with a second solid dielectric substance 8 at its flanks between the first solid dielectric substance 6 and the porous metallic electrode 3. The gases for reaction and an inert gas are supplied to the substrate 7 and the glow discharge plasma is generated under the pressure approximate to the atm. pressure. The excited active species are brought into contact with the substrate surface.



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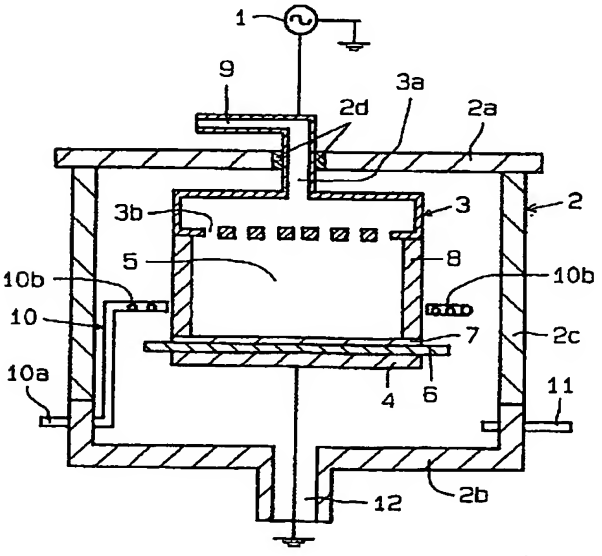
(54)【発明の名称】　基板の表面処理方法

(57)【要約】

【目的】　反応用ガスがプラズマ域に均一に拡散供給されその使用効率がよい、大気圧下でのグロー放電プラズマ法による基板の表面処理方法を提供する。

【構成】　金属電極４の一面に第１の固体誘電体６が設けられ、第１の固体誘電体６と対向して多孔金属電極３が設けられ、多孔金属電極３は反応用ガスを供給可能とされ、第１の固体誘電体６と多孔金属電極３の間は側面が第２の固体誘電体８で覆われた空間とされているプラズマ発生装置の、該空間内に基板７を設置して、基板７に不活性ガスと反応用ガスを供給し、大気圧近傍の圧力下で、グロー放電プラズマを発生させて、励起された活性種を基板表面に接触させる。



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【特許請求の範囲】

【請求項１】　金属電極の一面に第１の固体誘電体が設けられ、第１の固体誘電体と対向して多孔金属電極が設けられ、多孔金属電極は反応用ガスを供給可能とされ、第１の固体誘電体と多孔金属電極の間は側面が第２の固体誘電体で覆われた空間とされているプラズマ発生装置の、第２の固体誘電体で覆われた空間内に基板を設置して、基板に不活性ガスを供給すると共に、多孔金属電極を介して基板に反応用ガスを供給し、大気圧近傍の圧力下で、電極に電圧を与えてグロー放電プラズマを発生させて、そのプラズマによって励起された活性種を基板表面に接触させることを特徴とする基板の表面処理方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、例えば、プラスチック、紙、金属、ガラス、セラミックス等の基板の表面処理方法に関し、さらに詳しくは、大気圧近傍でのプラズマによる基板の表面処理方法に関する。

【０００２】

【従来の技術】従来より、例えば、プラスチック、紙、金属、ガラス、セラミックス等の基板の表面の濡れ性制御や表面修飾の方法として、０．１～１０Ｔｏｒｒ程度の低圧のグロー放電プラズマによる表面処理方法が広く知られており、産業的にも応用されている。この表面処理方法においては、上記の圧力よりも高い圧力になると、放電が局所的になりアーク放電に移行してしまい、耐熱性の乏しいプラスチックや紙のような基板への利用が困難となるので、通常、あらゆる基板に適用できるように上記の圧力範囲が選ばれている。このため、真空（もしくは低圧）にする必要上、処理用の容器は高価な真空チャンバーを必要とし、また真空排気装置が必要とされる。さらに、真空中で処理するため大面積の基板に処理しようとすると、大容量の真空容器を必要とし、真空排気装置も大型のものが必要である。そのため、設備費用が高くなるという問題点があった。また、吸水率の高い基板の表面処理を行う場合、真空にするのに長時間を要し、処理品がコスト高になるという問題点もあった。

【０００３】そこで、上記の種々の問題点を克服するために、装置、設備の低コスト化と、大面積基板への処理が可能な大気圧下でのグロー放電プラズマが提案されてきた。例えば、特開平２－１５１７１号公報には、電極表面に固体誘電体を配設する方法によって、特公平２－４８６２６号公報には、細線型電極を用いる方法によって大気圧下でグロー放電プラズマを行う表面処理方法が提案されている。これらの提案では、ヘリウムを主とする不活性ガスと反応用ガスとの混合ガスを、複数の開孔を有する多孔管から基板近傍のプラズマ域に供給する方法が用いられているが、この場合、大面積の基板になると均一にガスを拡散供給することが難しいという問題点があった。

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【０００４】また、特開平２－７３９７９号公報には、一方を対向面に多孔板状の固体誘電体を配設した表面処理用反応ガスを供給可能な金属電極とし、他方を金属電極とした、対向する２つの電極の間に基板を設置し、電極間の空間に不活性ガスと反応用ガスを供給し、大気圧近傍の圧力下で、電極に電圧を与えてグロー放電プラズマを起こさせ、そのプラズマによって励起された活性種を基板表面に接触させることによる、薄膜形成法が提案されている。しかしながら、この方法では、反応用ガスのうち実際に表面処理に使用されるガスの割合が少なく、未使用のガスが多量に発生し反応用ガスの使用効率（収率）が悪いという問題点があった。

【０００５】

【発明が解決しようとする課題】本発明は、上記の問題点に鑑みてなされたものであり、その目的は、反応用ガスがプラズマ域に均一に拡散供給されその使用効率がよい、大気圧下でのグロー放電プラズマ法による基板の表面処理方法を提供することにある。

【０００６】

【課題を解決するための手段】本発明の基板の表面処理方法は、金属電極の一面に第１の固体誘電体が設けられ、第１の固体誘電体と対向して多孔金属電極が設けられ、多孔金属電極は反応用ガスを供給可能とされ、第１の固体誘電体と多孔金属電極の間は側面が第２の固体誘電体で覆われた空間とされているプラズマ発生装置の、第２の固体誘電体で覆われた空間内に基板を設置して、基板に不活性ガスを供給すると共に、多孔金属電極を介して基板に反応用ガスを供給し、大気圧近傍の圧力下で、電極に電圧を与えてグロー放電プラズマを発生させて、そのプラズマによって励起された活性種を基板表面に接触させることを特徴とする。

【０００７】本発明において、基板の表面処理とは、主として、表面官能基層の形成やフリーラジカル層の形成や親水性や撥水性の薄膜を形成することなどによって、基板の表面エネルギーを制御し、基板の濡れ性や接着性を改質することや、基板表面に無機質や有機質の薄膜を形成させて、基板に化学的、機械的、光学的、電気的特性等を付与することを指す。

【０００８】本発明においては、表面処理の目的に応じて選択された反応用ガスを、多孔金属電極からプラズマ域に供給し表面処理を行う。反応用ガスとしては、例えば、基板表面にフッ素を化学結合させ表面エネルギーを低くし撥水性を付与する場合には、フッ素含有のガスを使用する。フッ素含有ガスとしては、４フッ化炭素（CF_4）や、６フッ化炭素（C_2F_6）等の飽和フッ化炭素ガスや６フッ化硫黄（SF_6）等のフッ化硫黄ガスが挙げられる。

【０００９】また、逆に表面エネルギーを高くし親水性を付与する場合には、表面にカルボニル基、ヒドロキシ

ル基、アミノ基等の官能基を有する層を形成させるために、炭化水素化合物のガスを使用する。上記炭化水素化合物としては、例えば、メタン、エタン、プロパン、ブタン、ペンタン、ヘキサン等のアルカン類；エチレン、プロピレン、ブテン、ペンテン等のアルケン類；ペンタジエン、ブタジエン等のアルカジエン類；アセチレン、メチルアセチレン等のアルキン類；ベンゼン、トルエン、キシレン、インデン、ナフタレン、フェナントレン等の芳香族炭化水素類；シクロプロパン、シクロヘキサン等のシクロアルカン類；シクロペンテン、シクロヘキセン等のシクロアルケン類；メタノール、エタノール等のアルコール類；アセトン、メチルエチルケトン等のケトン類；メタナール、エタナール等のアルデヒド類などが挙げられ、これらは、単独で使用されてもよいし２種以上併用されてもよい。また、この場合、酸素ガスや酸素と水素の混合ガスや水蒸気、アンモニアガス等を使用することも可能である。

【００１０】また、基板に化学的、機械的、光学的、電気的特性等を付与するために、SiO_2、TiO_2、SnO_2等の金属酸化物薄膜を形成する場合には、水素化金属ガス、ハロゲン化金属ガス又は金属アルコラート等の金属有機化合物のガスもしくは蒸気が用いられる。

【００１１】本発明に使用される基板は、材質、形状等は特に限定されず、プラスチック、金属、ガラス、セラミック、紙、繊維等が挙げられ、緻密でも多孔質でも構わない。プラスチックとしては、例えば、ポリエチレンテレフタレートやポリエチレンナフタレート等のポリエステル；ポリエチレン又はポリプロピレン等のポリオレフィン；ポリスチレン；ポリアミド；ポリ塩化ビニル；ポリカーボネート；ポリアクリロニトリル等のフィルムあるいはシートが使用できる。フィルムの場合、延伸されたものでも未延伸のものでも構わない。また、表面洗浄や表面活性化の公知の処理を行ったものでも構わない。

【００１２】以下にプラスチックの表面に撥水性を付与する場合を例に、図に基づいて本発明を詳細に説明する。なお、図１～３において、互いに対応するものには、同じ符号を付している。図１は、本発明に使用されるプラズマ発生装置の一例を示す模式断面図である。本装置は、電源部１、処理容器２、対向する多孔金属電極３と金属電極４、対向する２つの電極間のプラズマ処理部５から構成されている。電源部１はｋＨｚオーダーの周波数の電圧を印加可能とされており、撥水性を付与するには１０～３０ｋＨｚの周波数が好ましい。プラズマ形成は高電圧の印加によって行うが、印加電圧が低すぎるとプラズマ密度及びセルフバイアスが小さくなるので、処理に時間がかかり非能率的であり、高すぎるとアーク放電に移行する挙動を示すので、電界強度５～４０ｋＶ／ｃｍ程度になるように電圧を印加するのが好ましい。

【００１３】処理容器２は、上面２ａと底面２ｂがステンレス製、側面２ｃがパイレックスガラス製であり、上面２ａと多孔金属電極３との間に絶縁体２ｄが配設されている。処理容器２の材質は、これに限らず、全てがガラス製、プラスチック製でも構わないし、電極と絶縁がとれているならばステンレスやアルミニウム等の金属製でも構わない。

【００１４】本発明において、グロー放電プラズマによるプラズマ処理部５は、第１の固体誘電体と多孔金属電極の間の空間である。対向する電極は、少なくとも一方を対向面に第１の固体誘電体を配設した金属電極とし、少なくとも一方を反応用ガスを供給可能な多孔金属電極とする。すなわち、対向する２つの電極の構成としては、次の５つの場合がある。

①固体誘電体配設の金属電極－多孔金属電極
②固体誘電体配設の金属電極－固体誘電体配設の多孔金属電極
③金属電極－固体誘電体配設の多孔金属電極
④固体誘電体配設の多孔金属電極－多孔金属電極
⑤固体誘電体配設の多孔金属電極－固体誘電体配設の多孔金属電極

【００１５】図１では、上記①の構成が示されており、対向する２つの電極は、多孔金属電極３、第１の固体誘電体６を配設した金属電極４とから構成されている。反応用ガスを供給可能な多孔金属電極とは、多孔金属電極自体がガスの供給管を兼ねているものであり、図１の多孔金属電極３に示すように、電極の内部にガスの通路３ａが設けられており、対向する他方の電極に対する対向面が、ガスの出口部となる多数の開孔３ｂを有する多孔性の面とされているものである。なお、多孔金属電極３と金属電極４はどちらか一方が陽極側、他方が陰極側となるように接続される。また、上記①～⑤の構成の対向する２つの電極は、どちらが上部又は下部になっても構わない。

【００１６】プラスチック基板７は、第１の固体誘電体６の上に置かれる。なお、基板の片面のみの表面処理が必要ならば、前記の電極の構成のうち①～③が選ばれ、両面同時処理が必要ならば④又は⑤の構成が選ばれる。

【００１７】第１の固体誘電体６の材質としては、セラミック；ガラス；ポリテトラフルオロエチレンやポリエチレンテレフタレート等のプラスチックが用いられ、反応用ガスとの反応性によって適宜選択される。例えば、ガラスは４フッ化炭素プラズマによって容易に溶けてしまうので、撥水性付与の場合には用い難い。形状としては、シート状でもフィルム状でも構わないが、薄すぎると高電圧印加時に絶縁破壊が起こりアーク放電が生じ、また、厚すぎると放電しにくくなるため、０．０４～４ｍｍの厚みが好ましい。固体誘電体の配設は、対向面の一部に配設されない部分があるとその部分にアーク放電が生じるので、対向面の全面に配設される必要がある。

【００１８】対向する第１の固体誘電体と多孔金属電極の間の距離は、反応用ガスのガス流量、印加電圧の大きさ及び処理基板の厚み等によって適宜決定されるが、長すぎると対向する第１の固体誘電体と多孔金属電極の間の空間のガスの拡散の均一性が損なわれ、また、未使用の反応用ガスが多くなり非効率的であるため、１～２０ｍｍが好ましい。

【００１９】対向する第１の固体誘電体と多孔金属電極の配置構造としては、図１に示されるような互いに平行平板型以外にも、同軸円筒型、円筒対平板型、双曲面対平板型等でも構わないし、一方の電極の先端部が図２に示すように複数のパイプ状であっても構わないし、図３に示すように、複数の細線状であっても構わない。

【００２０】金属電極の材質は、ステンレスや真鍮等の多成分系の金属でも、銅、アルミニウム等の純金属でも構わない。

【００２１】本発明においては、対向する第１の固体誘電体と多孔金属電極の間の側面を第２の固体誘電体８で覆う。第２の固体誘電体の材質としては、前記した第１の固体誘電体に使用される材質と同様のものが挙げられるが、第１の固体誘電体と同じでも良いし異なっていてもよい。対向する第１の固体誘電体と多孔金属電極の間の側面を覆う方法としては、図１に示すように、第２の固体誘電体がシートのようにかなりの厚みを有する場合は、第２の固体誘電体と接触する基板表面は処理不可能となるため、処理される基板の処理予定領域よりも大きくシートをくり抜き、基板の処理予定領域がくり抜かれた内部に入り得るようにした状態で、該シートを対向する第１の固体誘電体と多孔金属電極の間に挟み込む方法、図２又は図３に示すように第２の固体誘電体がフィルムの場合は電極の外周面にスカート状に巻き付ける方法が挙げられる。

【００２２】第２の固体誘電体によって、第１の固体誘電体と多孔金属電極の間の側面が密閉されればされるほど反応用ガスは効率よく使用されるが、不活性ガスと反応用ガスを異なった入り口から処理容器２に供給する場合は、不活性ガスをプラズマ処理部５に拡散させるために充分な隙間を開けておく必要がある。隙間を形成させる方法としては、例えば、第２の固体誘電体８の側面に小さな孔を開ける方法、第２の固体誘電体８が上記のシートのような場合はシート上面又は下面に凹凸を設ける方法などが挙げられる。

【００２３】本発明においては、前述のように、前記第１の固体誘電体と多孔金属電極の間に基板７を設置し、前記空間に不活性ガスと反応用ガスを供給し、大気圧近傍の圧力下で、電極に電圧を与えてグロー放電プラズマを起こさせ、そのプラズマによって励起された活性種を基板表面に接触させる。

【００２４】上記、大気圧近傍の圧力とは、１００～７７０Ｔｏｒｒのことを指し、装置、設備の低コスト化を考慮すると大気圧が好ましい。

【００２５】不活性ガスとしては、Ｈｅ、Ｎｅ、Ａｒ、Ｘｅ等の希ガスや窒素ガスの、単体又は混合ガスが用いられるが、準安定状態の寿命が長く反応用ガスを励起分解するのに有利なＨｅを用いるのが好ましい。Ｈｅ以外の不活性ガスを使用する場合は、２体積％以内のアセトンやメタノール等の有機物蒸気やメタン、エタン等の炭化水素ガスを混合する必要がある。

【００２６】撥水性を付与する場合は、反応用ガスとしては、フッ素含有のガスが使用される。不活性ガスとフッ素含有ガスとの混合比は、フッ素含有ガス濃度が約１０体積％以上では高電圧を印加してもグロー放電プラズマが発生し難いため、約１０体積％以下が好ましく、反応ガスの使用量が少なくてすみ、且つ撥水性を付与可能な０．３～５．０体積％の間がより好ましい。

【００２７】反応用ガスは、マスフローコントローラーで流量制御されプラズマ処理部５に多孔金属電極３のガス導入口９から導入される。不活性ガスは、ガス導入管１０のガス導入口１０ａから、マスフローコントローラーによって流量制御され処理容器２に導入される。ガス導入管１０は、処理容器２内の部分が、図１に示すように、プラズマ処理部５の周囲を取り巻くようにされ、その取り巻かれた部分の内周面に多数の孔が開けられ、その孔をガス出口１０ｂとされてもよいが、特にこのように構成せずとも不活性ガスはプラズマ処理部５にほぼ均一に拡散される。また、不活性ガスと反応用ガスを混合してガス導入口９から導入しても構わないが、均一に撥水性を付与するためには、反応用ガスのみをガス導入口９から導入するのが好ましい。尚、未使用の反応用ガス、不活性ガスは処理容器の気体排出口１１から排出される。

【００２８】撥水性付与の大気圧プラズマ処理には基板の加熱や冷却は、特には必要なく室温下で十分可能である。

【００２９】また、処理時間は印加電圧の大きさで決定され、前記印加電圧の範囲では５秒程度で撥水化されておりそれ以上の時間をかけて処理しても撥水化効果は向上せず、短時間の処理で十分である。

【００３０】

【実施例】以下、本発明の実施例を説明する。

実施例１

図１に示したプラズマ発生装置（金属電極４は直径８０ｍｍの円板型とし、その上に第１の固体誘電体６として直径９０ｍｍ、厚み１ｍｍのポリテトラフルオロエチレンを配設。多孔金属電極３は対向面の直径８０ｍｍの円板型）に於いて、基板７として８０ｍｍ×８０ｍｍ×厚み１００μｍのポリエステルフィルム（東レ社製、商品名「ルミラーＳ１０」）を、第１の固体誘電体６上に置き、その基板７上に、対向する第１の固体誘電体と多孔金属電極の間の側面を覆う第２の固体誘電体８として外

径８０mm、内径７０mm、厚み５mmの波板状のポリテトラフルオロエチレンシートを置き（シートが波板状なので、基板７と第２の固体誘電体８の間、及び、多孔金属電極３と第２の固体誘電体８の間には、僅かの隙間が形成される）、基板７と多孔金属電極３の距離を約５mmに設定後、１Ｔｏｒｒまで油回転ポンプ（図示せず。以下同じ）で排気口１２より排気した。

【００３１】次いで、ガス流量２ｓｃｃｍの４フッ化炭素ガスをガス導入口９より、また、１９８ｓｃｃｍのＨｅガスをガス導入口１０ａより処理容器２内に導入し、７６０Ｔｏｒｒの大気圧とした後、周波数１５ｋＨｚの矩形波を、６．２ｋＶ、２８mＡの電力で印加し１０秒間放置して、基板の表面処理をした。高電圧印加にともなって、プラズマ発光が観察され、その時の、電圧－電流特性をオシロスコープで観察した結果、図４に示したパルス特性を示し、半サイクルに単一パルスの電流特性の典型的なパルス放電であることが分かった。

【００３２】次に、処理後の基板の処理面の純水に対する接触角測定を行った。その結果、直径６０mmの円領域で１００～１０８度を示し撥水化されていることが明らかであった。尚、使用した基板の接触角は６５度であった。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で６７％のフッ素が表面に化学結合していることが分かった。

実施例２

実施例１における、第２の固体誘電体８として厚み５mmの波板状のポリテトラフルオロエチレンシートを使用したこと、及び基板７と多孔金属電極３の距離を約５mmに設定したことの代わりに、それぞれ厚み１０mmの波板状のポリテトラフルオロエチレンシートを使用したこと、及び基板７と多孔金属電極３の距離を約１０mmに設定したこと、並びに実施例１におけるガス流量、電力及び処理時間を下記のように変えたことの他は、実施例１と同様にして基板の表面処理をした。ガス流量６ｓｃｃｍの４フッ化炭素ガスをガス導入口９より、また、１９４ｓｃｃｍのＨｅガスをガス導入口１０ａより処理容器２内に導入し、７６０Ｔｏｒｒの大気圧とした後、周波数１５ｋＨｚの矩形波を、１０．０ｋＶ、３５mＡの電力で印加し１０分放置して、基板の表面処理をした。

【００３３】その結果、高電圧印加にともなってプラズマ発光が観察され、処理後の基板の処理面の純水に対する接触角は、直径６０mmの円領域で１００～１０８度を示し撥水化されていることが明らかであった。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で６５％のフッ素が表面に化学結合していることが分かった。

【００３４】実施例３

多孔金属電極３の先端部が複数のパイプ状をしている図２に示した構造の電極（多孔金属電極の対向面は、直径８０mmの円形であり、８０本の長さ１０mm、外径２mm、内径１mmのパイプ３ｃが突設している）とし、金属電極４は直径８５mmの円板型とし、その上に第１の固体誘電体６として直径９０mm、厚み１mmのポリテトラフルオロエチレンを配設した装置を使用し、基板７として８５mm×８５mm×厚み１２μmのポリアミドフィルム（東レ社製、商品名「カプトン」）を、第１の固体誘電体６上に置き、次いで多孔金属電極３の外周面を第２の固体誘電体８である厚み１００μmのポリテトラフルオロエチレンフィルムでスカート状に覆った後（多孔金属電極３の対向面からスカートの先端までの長さは２０mmとした）、基板７と多孔金属電極３のパイプ３ｃの先端までの距離を約５mmに設定後、１Ｔｏｒｒまで油回転ポンプで排気した。次いで、ガス流量４ｓｃｃｍの４フッ化炭素ガスをガス導入口９より、また、１９４ｓｃｃｍのＡｒガスと２ｓｃｃｍのアセトン蒸気との混合ガスをガス導入口１０ａより処理容器２内に導入し、７６０Ｔｏｒｒの大気圧とした後、周波数１５ｋＨｚの矩形波を、１２．５ｋＶ、３８mＡの電力で印加し１０秒間放置して、基板の表面処理をした。高電圧印加にともなって、プラズマ発光が観察された。

【００３５】処理後の基板の処理面の純水に対する接触角は、直径８５mmの円領域で１００～１０８度を示し撥水化されていることが明らかであった。尚、使用した基板の接触角は６３度であった。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で５５％のフッ素が表面に化学結合していることが分かった。

【００３６】比較例１

実施例１における、基板７上に第１の固体誘電体と多孔金属電極の間の空間を覆う第２の固体誘電体８としてのポリテトラフルオロエチレンシートを置かなかったこと及び４フッ化炭素ガスをガス導入口９より、また、Ｈｅガスをガス導入口１０ａより処理容器２内に導入したことの代わりに、４フッ化炭素ガスとＨｅガスを混合してガス導入口１０ａより処理容器２内に導入したことの他は、実施例１と同様にして基板の表面処理をした。

【００３７】その結果、高電圧印加にともなってプラズマ発光が観察され、処理後の基板の処理面の純水に対する接触角は、あらゆる処理面で３０度以下の接触角を示し撥水化されていないことが分かった。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で５％程度のフッ素しか表面に化学結合していないことが分かった。

【００３８】比較例２

比較例１で４フッ化炭素ガスとＨｅガスを混合してガス導入口１０ａより処理容器２内に導入したことの代わりに、４フッ化炭素ガスとＨｅガスとの混合ガスをガス導入口９より処理容器２内に導入したことの他は、比較例１と同様にして基板の表面処理をした。その結果、高電圧印加にともなってプラズマ発光が観察され、処理後の

基板の処理面の純水に対する接触角は、あらゆる処理面で３５～４５度の接触角を示し撥水化されていないことが分かった。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で２０％程度のフッ素しか表面に化学結合していないことが分かった。

【００３９】実施例４

実施例１で４フッ化炭素ガスをガス導入口９より、また、Ｈｅガスをガス導入口１０ａより処理容器２内に導入したことの代わりに、４フッ化炭素ガスとＨｅガスを混合してガス導入口９より容器内に導入したことの他は、実施例１と同様にして基板の表面処理をした。その結果、処理後の基板の処理面の純水に対する接触角は、４５～１０８度の間でばらついた。また、処理面を、Ｘ線電子分光法で分析した結果、原子比で２０～６０％の化学結合したフッ素が確認された。

【００４０】実施例５

実施例１で、基板としてポリエステルフィルムを用いたことの代わりに、濾紙を用いたことの他は、実施例１と同様にして表面処理を行った。その結果、処理後の基板の処理面の純水に対する接触角は、直径６０mmの円領域で１００～１０８度を示し撥水化されていることが明らかであった。

【００４１】実施例６

多孔金属電極３の先端部が複数の細線状をしている図３に示した構造の電極（多孔金属電極の対向面は、直径８０mmの円形であり、長さ１０mmの細線３ｄが、１０本／ｃｍ² の密度で突設している）とし、金属電極４は直径８５mmの円板型とし、その上に第１の固体誘電体６として直径９０mm、厚み１mmのポリテトラフルオロエチレンを配設した装置を使用し、基板７として８５mm×８５mm×厚み１００μmのポリエステルフィルム（東レ社製、商品名「ルミラーＳ１０」）を、第１の固体誘電体６上に置き、次いで多孔金属電極の外周面を第２の固体誘電体８である厚み１００μmのポリテトラフルオロエチレンフィルムでスカート状に覆った後（多孔金属電極３の対向面からスカートの先端までの長さは２０mmとした）、基板７と多孔金属電極３の細線３ｄの先端までの距離を約５mmに設定後、１Ｔｏｒｒまで油回転ポンプで排気した。

【００４２】次いで、ガス流量１ｓｃｃｍの４フッ化炭素ガスと２ｓｃｃｍの酸素との混合ガスをガス導入口９より、また、１９７ｓｃｃｍのＨｅガスをガス導入口１０ａより処理容器２内に導入し、７６０Ｔｏｒｒの大気圧とした後、周波数１５ｋＨｚの矩形波を、６．２ｋＶ、２８mＡの電力で印加し３０秒間放置して、基板の表面処理をした。高電圧印加にともなって、プラズマ発光が観察された。処理後の基板の処理面の純水に対する接触角は、直径８５mmの円領域で１５度を示し親水化されていることが明らかであった。

【００４３】

【発明の効果】本発明の構成は上述の通りであり、従来の低圧グロー放電プラズマによるプラスチック等の表面処理方法にくらべて、特別な真空形成のための装置・設備が必要でなく、しかも、そのための特別な操作も不必要であり、コスト低下効果に優れ、かつ、取扱は容易である。また、反応用ガスがプラズマ域に均一に拡散供給されるので、大気圧プラズマの課題であった処理領域の大面積化が可能であり、また、反応用ガスの効率的利用が可能である。さらに、基板の両面を同時に表面処理可能である、また、処理面の領域指定も可能であり、今後産業上の波及効果は大きい。さらに、薄膜形成にも容易に展開可能である。

【図面の簡単な説明】

【図１】図１は、本発明の表面処理方法に使用されるプラズマ発生装置の一例を示す模式断面図である。

【図２】図２は、多孔金属電極の構造の変形例とその使用方法を示す模式断面図である。

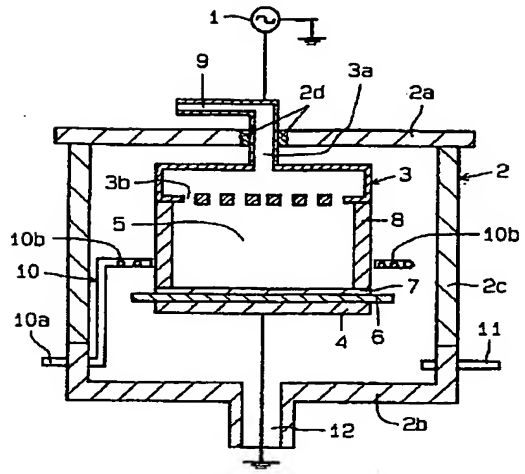
【図３】図３は、多孔金属電極の構造の変形例とその使用方法を示す模式断面図である。

【図４】図４は、実施例１の電圧－電流のパルス特性を示すグラフである。

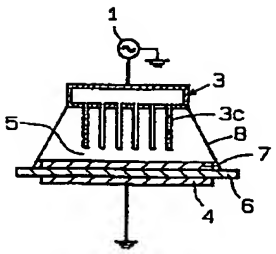
【符号の説明】

１　電源
２　処理容器
２ａ　上面
２ｂ　底面
２ｃ　側面
２ｄ　絶縁体
３　多孔金属電極
３ａ　ガスの通路
３ｂ　開孔
３ｃ　パイプ
３ｄ　細線
４　金属電極
５　プラズマ処理部
６　第１の固体誘電体
７　基板
８　第２の固体誘電体
９　ガス導入口
１０　ガス導入管
１０ａ　ガス導入口
１０ｂ　ガス出口
１１　気体排出口
１２　排気口

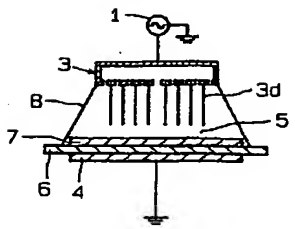
【図１】


1
9
3a
2d
2a
2
3b
3
5
8
10b
10b
10
7
2c
10a
4
6
11
12
2b

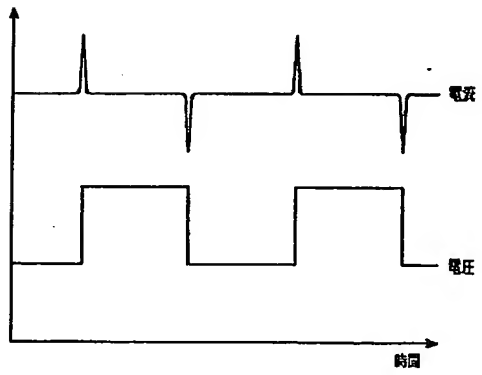
【図２】


1
3
3c
5
8
7
6
4

【図３】


1
3
3d
8
5
7
6
4

【図４】


電荷
電圧
時間